Velocity of Thermal Decomposition of Carbonates

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Velocity of Thermal Decomposition of Carbonates

A DISSERTATION

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VELOCITY OF THERMAL DECOMPOSITION OF CARBONATES*

BY B. BRUŽS[1]

The problem of the thermal decomposition of carbonates has been undertaken with two objects in view. Firstly to bring some light on the question why many of the heterogeneous equilibria between solid substances and gases can be attained only by way of decomposition, the equilibrium pressures not being regained when the reaction is reversed. Secondly the kinetics themselves promised to give interesting results regarding the influence of temperature on reaction velocities, as previous experience with some carbonates showed that the process of decomposition could often be interpreted by means of the usual homogeneous reaction equations.

The classical theory of a dynamic equilibrium for solid-gaseous systems in general and carbonates-carbon dioxide and salt-hydrates-water vapor in particular is mainly due to the early work of C. L. Berthollet[2], H. Rose[3], H. Sainte-Claire Deville, Debray[4], and Pfaundler[5].

The general conclusion of this work can be summarized as follows. At equilibrium, the velocities of decomposition and recombination are equal and, therefore, the pressure of the gaseous phase is determined by the temperature. Ample experimental proof was accumulated by the same authors to show the catalytic activity of water in the case of the thermal decomposition of carbonates.

The question has obtained its thermodynamic solution in the "exact" formula of Nernst for calculation of equilibrium constants of chemical reactions and, in a special case, the "approximation formula" of Nernst for the equilibrium constant for a carbonate

$$\log p = -Q/4.571T + 1.75 \log T + 3.2$$

enables one to determine approximate carbon dioxide pressures for any carbonate from the knowledge of the heat of the reaction

$$MeO + CO_2 = MeCO_3 + Q.$$

But, some very large discrepancies in the experimental determinations of carbon dioxide pressures and theoretical considerations (Langmuir) have cast doubts on the validity of the kinetic explanation of the equilibrium. Nernst has introduced in his work the idea of the equilibrium taking place in the gaseous phase, where all components are supposed to be present in the form of their saturated vapor. Ostwald has called attention to the improbability of such an assumption. It is difficult to imagine substances like calcium oxide having appreciable vapor pressure.

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* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Charlotte Elizabeth Procter Fellow.

[2] Essaide Statique chimique, 48-53 (1803).

[3] Pogg. Ann., **82**, 545 (1851); **55**, 415 (1842).

[4] Compt. rend., **64**, 603 (1867); **79**, 890 (1874).

[5] Pogg. Ann., **131**, 55 (1867); Jubelband 182 (1874).

Another explanation which would replace the mechanisms of Berthollet and Nernst was given by Langmuir[1], who proposed the idea of a reaction taking place at an interface metal oxide-metal carbonate or salt hydrate-salt respectively.

No extensive investigations have been made of the velocities in question. The first case was studied by G. N. Lewis[2], who investigated the decomposition of silver oxide and found the reaction to obey the equation of an autocatalytic reaction, where silver plays the rôle of the catalyst. But, his final conclusion was that he really measured the velocity of the reaction $2O = O_2$ in presence of silver. Hinshelwood and Bowen[3] and Hinshelwood[4] investigated a number of substances, most of them of an explosive character and are inclined to believe in interface reactions. Some analogous results in cases of mostly autoaccelerated reactions have been obtained by Sieverts and Thieberath[5], Otto and Fry[6], and Crowther and Coutts[7]. Reaction velocities not showing acceleration have been described by Centnerszwer and Bružs[8].

The Apparatus

The main aim of the apparatus employed is to investigate the reaction from its very beginning and secondly to conduct it at constant temperature and pressure. Fig. 1 gives a schematic idea of the apparatus.

The substance is placed in the reaction vessel A, a narrow glass tube and connected through the ground seal B to the gasholder C, an iron vessel of large size. On account of the largeness of the vessel the gas remains practically at the original pressure when not more than 100 ccm. of gas are collected in it. The gasholder is kept at constant temperature (25°) in a thermostat K. This arrangement permits an investigation of the reaction at different pressures, although most of the experiments in this investigation have been conducted at atmospheric pressure. Through the stopcock F the apparatus is filled with carbon dioxide. When the reaction takes place, the gas pressing on the surface of the mercury in C causes mercury to flow over in D. The overflowing mercury is collected in E and gives a measure of carbon dioxide evolved in the reaction. G is an iron block, the furnace, heated by nichrome wire wound around it. It has two drilled holes, just fitting the reaction vessel and the thermometer I. Besides that there is a larger hole (not shown in Fig. 1) for a larger reaction vessel. The furnace is very carefully insulated with asbestos and magnesia, so that for temperatures up to 700° it does not require more than 1.5 amps. (at 110 volts) and makes hand regulation with an ammeter and resistance very easy. The temperature in the experiments very seldom fluctuated more than ± 0.1°.

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[1] J. Am. Chem. Soc., **38**, 222 (1916).
[2] Z. physik. Chem., **52**, 310 (1905).
[3] Phil. Mag., (6), **40**, 569 (1920); Proc. Roy. Soc., **99A**, 203 (1921).
[4] J. Chem. Soc., **119**, I, 721 (1921).
[5] Z. physik. Chem., **100**, 463 (1922).
[6] J. Am. Chem. Soc., **45**, 1134 (1923).
[7] Proc. Roy. Soc., **106A**, 215 (1924).
[8] Acta Univ. Latviensis **11**, (1924); Z. physik. Chem., **115**, 365 (1925); J. Phys. Chem., **29**, 733 (1925).

The Velocity of Decomposition of Ferrous Carbonate

From the number of carbonates investigated in this research with respect to their velocities of thermal decomposition the crystalline natural siderite can be described first on account of the simplicity of this process. The velocity of decomposition of very pure large crystals of siderite of about 0.4 gr. has been measured in the range of 491°-581°C. The decrease of the velocity of carbon dioxide evolution with time clearly showed that the process can be described by the formula of a unimolecular reaction.

For the sake of simplicity and convenience the following method of calculation has been applied. The volume of carbon dioxide evolved during fixed intervals of time (1/2 min.-20 min., depending on the temperature of the experiment) was accepted as a measure of the velocity of decomposition in the interval. The velocity of a unimolecular reaction decreases with time according to the formula:

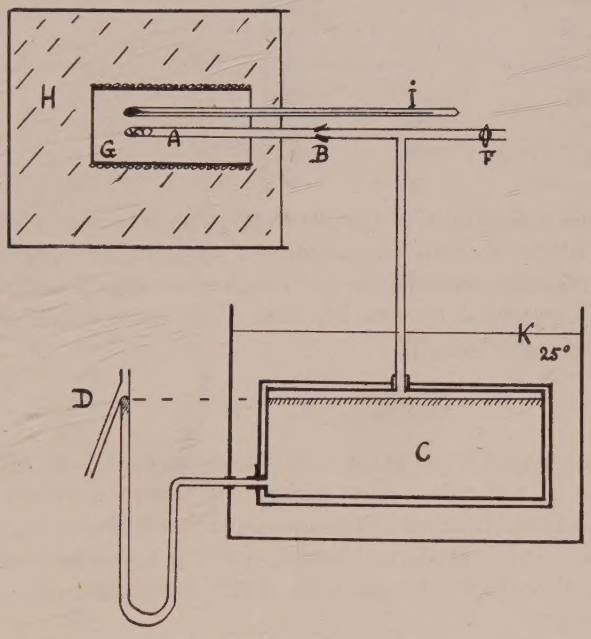

FIG. 1

$$I_t = I_o e^{-\lambda t}$$

where I_t is the velocity at the moment t, I_o the initial velocity and λ the reaction constant.

From this equation the following relation is easily derived

$$\lambda = \frac{\ln I_{t_1} - \ln I_{t_2}}{t_2 - t_1}$$

in words: the slope of the straight line representing the plot of the logarithms of the velocities against time gives the constant of the reaction.

In fact the data of all experiments except the one experiment at the lowest temperature (491°) when plotted in the way mentioned above gave straight lines. The constants[1] of the reaction for the different temperatures obtained by this calculation are given in Table I.

TABLE I

C°	λ	λ calc.
491	.00805	
501	.0106	.011
511	.0221	.022
521	.0442	.044
531	.0851	.085
540	.154	.150
541	.191	.180
550	.352	.290
553	.301	.350
561	.607	.580
566	.667	.780
573	.989	1.18
581	1.472	1.90

When the logarithms of the reaction constants were plotted against the reciprocals of the absolute temperature a straight line resulted, which meant that the Arrhenius formula for the relation between reaction constants and temperature was valid for this reaction. The value of the critical increment E of the Arrhenius formula

$$E = \frac{R}{T_2^{-1} - T_1^{-1}} \cdot \ln \frac{\lambda_{T_1}}{\lambda_T^2}$$

has been calculated from the reaction constants at 501° and 561°. E was found to be 85,500 cals. How closely the observed values agree with the values recalculated from the Arrhenius equation is shown by the third column of the table. Table II shows the calculated percentage decomposition compared with the observed values for eight experiments in a wide range of temperature.

A marked deviation can be seen in the two latter experiments, but one must take into consideration that a deviation of 15 percent is not too high for a reaction the half-lifetime of which is 0.58 min.

Two further questions were investigated in connection with the decomposition of siderite.

As has been noted above, the experiment for the lowest temperature gave an abnormal value for the velocity constant. To settle this question 5 experiments were conducted at low temperatures with large siderite crystals (3-4 grams). In all cases the velocities had very low values and the plots of

[1] All constants are calculated with the use of natural logarithms and are given in reciprocal minutes. Time is given in minutes.

TABLE II

501° time	% decomposed calc.	obs.	511° time	% decomposed calc.	obs.	521° time	% decomposed calc.	obs.
20	20	22	10	20	22	5	20	20
40	36	38	20	36	38	10	36	36
60	48	50	30	48	49	15	48	48
80	59	59	40	59	59	20	59	58
100	67	67	50	67	67	25	68	66
120	73	73	60	73	73	30	74	72
140	79	79	70	79	78	35	79	
160	83	83	80	83	82	40	84	82
180	86		90	86	86	45	87	86
			100	89		50	90	90

531° time	% decomposed calc.	obs.	541° time	% decomposed calc.	obs.	553° time	% decomposed calc.	obs.
2	16	16	1	16	16	1	30	28
4	29	29	2	30	30	2	50	49
6	40	40	3	42	42	3	65	63
8	49	50	4	51	51	4	75	74
10	57	58	5	59	59	5	83	81
12	64	64	6	66	66	6	88	87
14	70	70	7	72	71	7	91	91
16	74	75	8	76	76	8	94	94
18	78	79	9	80	79	9	96	
20	82	82	10	84	82	10	97	97
22	85		15	93	91	11	98	98
24	87		20	97	94	12	99	99
26	89	88						

561° time	% decomposed calc.	obs.	573° time	% decomposed calc.	obs.
0	44	33	0.5	45	36
1	69	57	1.0	69	63
2	82	75	1.5	83	79
3	90	86	2.0	91	86
4	95	93	2.5	95	92
5	97	96	3.0	97	95
6	98	98	3.5	98	
7	99	99	4.0	99	99

the logarithms of the velocities against time showed indeed a linear course; but, one could readily see that the velocity of carbon dioxide evolution would reach zero before the substance would be totally decomposed. Still, the slope

of the curve was calculated as by this process we eliminate the time factor. The percentage decomposition which could be achieved if the reaction were continued until the velocity had reached zero can then be readily extrapolated from the slope of the curve and the initial velocity I_o as

$$I_o = \lambda N \text{ and } N = I_o/\lambda$$

If we give the value of N so obtained a meaning of "active mass" then λ becomes the reaction constant. Table III gives these values.

TABLE III

C°	λ	N
445	.0035	
455	.0064	9 percent
465	.0058	14 "
485	.0058	50 "
495	.0074	100 "

We must draw from these experiments the conclusion that in the range of temperature between 455°-495° the velocity constant of the reaction remains practically constant and only the active mass increases with temperature. Above 495° the active mass reaches the value of 100 percent.

It is worth while noting at this place that the samples of the siderite after this partial decomposition were investigated with respect to interface formation, but, it was found that even the largest and least decomposed samples had turned black uniformly throughout the whole crystal.

The second question investigated concerned the dependence of the reaction constant upon the state of grinding. Crystals from the same batch of siderite that had been used in the previous experiments were ground and sieved through screens; a uniform fraction of powder was collected between two screens of close mesh number and used for five experiments. The average size of the crystals measured under the microscope was 0.3 mm. The curves representing the plot of the logarithms of the velocity against time again showed a straight line relationship and the reaction constants could be easily calculated. They are given in Table IV.

TABLE IV

C°	λ	
485	.0065	N = 60 percent
495	.0065	
505	.0166	
515	.0414	
525	.0966	

Here again we see the same fact that the reaction constant for temperatures below 495° is too high, namely at 485° it is as high as the reaction constant at 495° but, as in the previous case, the reaction does not tend to go to completion. The "active mass" is only 60 percent.

The constants for the four experiments carried out at temperatures at and higher than 495° lie on a straight line, when their logarithms are plotted against the reciprocal absolute temperature. The critical increment is higher than in the reaction with a single crystal, it is 110,800 cals..

It must be mentioned that the velocity of a small part of the initial stage of the reaction exceeds the values to be expected from the greater part of the reaction. This small deviation seems to be due to small amounts of very fine dust of broken crystals. This observation is in accord with the higher value for the critical increment found with the smaller crystals.

Velocity of Decomposition of Synthetic Ferrous Carbonate

Synthetic ferrous carbonate has been prepared by the method of Sénarmont, by the action of a concentrated ferrous chloride solution on calcium carbonate at 170°. The carbonate obtained, when dried, lost, together with the water, about 20 percent of its carbon dioxide. It readily dissolved in cold acids.

Nevertheless, some experiments carried out with this preparation which did not yield any definite results, still gave an idea about the velocity of decomposition, and mainly the important fact that decomposition at 760 mm. carbon dioxide was complete at 340° as compared with a temperature of 495° for the naturally occurring mineral.

Below 340° the decomposition is not complete and the reaction velocity is of the order of .004-.006 min.$^{-1}$. Three experiments above 340° gave better results. The constants obtained were

340°	.0110
350°	.0152
360°	.0239

and their logarithms when plotted against the reciprocal absolute temperature gave a straight line, which permitted one to calculate the critical increment 30,700.

The Velocity of Decomposition of Cobaltous Carbonate

Cobaltous carbonate has been prepared in a dry and crystalline state by the action of a saturated cobaltous chloride solution during twenty-four hours on calcium carbonate powder in a sealed tube at 170°C. This method of synthesis, described by Sénarmont[1] has been applied because simple drying of the common carbonate in a stream of carbon dioxide does not yield the anhydrous carbonate. The crystalline anhydrous cobaltous carbonate is reminiscent of some natural carbonates by reason of its very slow solubility in acids.

The results of a series of 5 experiments made at temperatures ranging from 427°C. to 477°C. were plotted in the following way. The scale of the abscisse (time) has been increased by 100 percent for every succeeding experiment, which is always made at 10° higher than the preceding one. The

[1] Ann. Chim. Phys., (3) **30**, 138 (1850).

ordinate represents the percentage of cobaltous carbonate decomposed. Under these conditions the initial course of the curve falls together for all experiments. The further run of the curve shows marked divergencies. In other words, the temperature coefficient for the initial stage of the reaction is very close to 2 for a 10° rise and is higher than two in the final stage.

The course of the individual curves has been analysed by plotting the logarithms of the reaction velocity against time and it has been found that the curve obtained is a straight line for the initial stage of the reaction, changes quite abruptly its slope at a certain point and continues then again as a line up to the end of the reaction. The same characteristic behaviour is shown by the plot of the reaction velocity against the percentage of decomposition.

This observation and previous experience with analogous curves lead to the conclusion that the decomposition takes place in two stages and most probably according to the scheme:

$$CoCO_3 \longrightarrow CoCO_3 \,.\, CoO + CO_2$$
$$CoCO_3 \,.\, CoO \longrightarrow CoO + CO_2.$$

This theory would further account for the fact that the temperature coefficient as mentioned above is about 2 in the first stage and higher for the second half of the reaction, the cause being that the first stage represents the first and fast reaction, the rest of the curve the second and slow reaction. The second reaction begins at higher temperature and would naturally be expected to have a higher temperature coefficient as the temperature coefficient, with other conditions maintained the same, decreases with increase of temperature.

To test the assumption, the experimental data have been compared with values theoretically to be expected. The constant of the first reaction has been evaluated from the initial velocity of the reaction, where the second reaction does not yet play an appreciable rôle. This can be done by the use of the formula

$$I = N\lambda_1 \qquad \text{and} \qquad \lambda_1 = I/N,$$

where I is the velocity of the reaction in percent per minute, λ_1 the reaction constant and N the active mass, here according to our assumption 50 percent (carbon dioxide). The constant of the final reaction has been evaluated from the final slope of the curve representing the plot of the logarithms of the velocities against time, here

$$\lambda_2 = \frac{\ln I_1 - \ln I_2}{t_2 - t_1}$$

where t is the respective time. Both constants then have been substituted in the theoretical equation for the assumed reactions:

$$CO_2 = \frac{a}{2}\left(2 + \frac{2\lambda_2 - \lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_1 t} - \frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_2 t}\right)$$

where CO_2 means the percentage of the total amount of carbon dioxide (a) evolved at the time t from the beginning of the reaction and λ_1 and λ_2 are the reaction constants of the first and second reactions respectively. The agreement between observed and calculated values can be seen from Table V.

TABLE V

447°
$\lambda_1 = .018$ $\lambda_2 = .0023$

time	% decomposed obs.	calc.
50	34	32
100	47.8	48
150	57.5	57
200	64.0	63
250	68.0	68
300	71.6	72
350	74.2	75
400	76.0	78

457°
$\lambda_1 = .040$ $\lambda_2 = .0055$

time	% decomposed obs.	calc.
20	28.7	28
40	42.0	44
60	51.2	54
80	58.5	61
100	63.8	65
120	68.3	70
140	72.3	72
160	75.5	75

467°
$\lambda_1 = .0805$ $\lambda_2 = .0115$

time	% decomposed obs.	calc.
10	29.6	29
20	44.0	41
30	54.7	55
40	62.8	62
50	68.6	66
60	73.8	70
70	77.5	74
80	80.6	76
90	83.1	80
100	85.1	82
110	86.7	84
120	88.2	85
150	91.0	90
360	99.5	99

477°
$\lambda_1 = .138$ $\lambda = .023$

time	% decomposed obs.	calc.
10	41.8	42
20	62.1	60
30	73.9	69
40	81.3	76
50	85.1	81
60	88.0	85
70	90.1	88
80	91.6	90
90	92.9	92
100	94.0	94
110	94.8	95
120	95.5	96
130	96.1	97
140	96.5	98
150	96.9	98

These values permit one to calculate the critical increment of the reactions, as, in the observed range of temperature, the constants of both reactions show a linear relation between the logarithms of the reaction constants and the reciprocal of the absolute temperature. From

$$E = \frac{R}{T_2^{-1} - T_1^{-1}} \cdot \ln \frac{\lambda_{T_1}}{\lambda_{T_2}}$$

we find, substituting the values determined above the critical increments E_1 and E_2 for the first and second reactions

$$E_1 = 72{,}400$$
$$E_2 = 82{,}200$$

The Velocity of Decomposition of Zincspar

A series of thirteen experiments was conducted in the range of 407°-452°C. The substance used for these experiments was very pure natural "amorphous" zincspar; the carbon dioxide evolved in the experiments was always in close agreement with theoretical values for total decomposition.

The velocity of decomposition showed a peculair behaviour: about 65 percent of the substance was decomposed at a practically constant rate; after that, the reaction markedly slowed down and abruptly finished near the end.

No mathematical expression could be found to describe this reaction neither by postulating intermediate reaction, nor assuming a heterogeneous catalysis by zinc oxide.

The only way to find the influence of temperature was to compare the constant velocities of the main part of the reaction referred in each case to 1 gr. of carbonate. The amount of substance used in the experiments was 0.5-0.8 gr. in each run. The combined data are given in Table VI. Column 3 gives the percentage decomposition up to which the reaction velocity is constant.

TABLE VI

°C	Const.	Validity
407	.22 cm/min	38 percent
417	.49	71
423	1.94	58
427	2.54	72
427	2.35	67
430	2.60	83
432	2.23	65
437	3.84	66
437	7.13	74
438	3.32	68
442	6.66	60
447	14.65	79
452	11.50	61

The data do not give a good agreement and the deviations of the determined values from a continuous increase of this value with temperature exceed the experimental error.

A straight line drawn through the logarithms of the velocities plotted against the reciprocal of the absolute temperature gave a value of the critical increment 95,000.

When the reaction was finished the lumps of zinc carbonate were not broken and were yellow when hot and white when cool.

The Velocity of Decomposition of Cerussite

The thermal decomposition of lead carbonate represents the most complicated example of the reactions investigated here. This fact could be expected from carbon dioxide pressure measurements of lead carbonate described by Centnerszwer, Falk, and Awerbuch[1], which lead the authors to conclude that three intermediate compounds $3 . PbO . 5PbCO_3$; $PbO . PbCO_3$; $2PbO . PbCO_3$ are formed in the course of the decomposition.

A large number of experiments was conducted with two different samples of crystalline natural lead carbonate. The results checked satisfactorily for experiments conducted in the range from 320°-350°C. with beautifully developed single crystals of cerussite weighing from 0.6-0.9 grams each. In all cases 50 percent of the total amount of carbon dioxide were evolved, which fact proves the formation of the intermediate compound $PbO . PbCO_3$, described by M. Centnerszwer, Falk and Awerbuch as stable in this range of temperature. The mathematical analysis of the decomposition curves showed that the reaction obeyed the scheme of a unimolecular reaction.

TABLE VII

°C	λ
320	0.0046
325	.0069
330	.0110
335	.0173
340.3	.0308
345.3	.0478
350	.1007

The logarithms of the reaction constants plotted against the reciprocal absolute temperature lay on a straight line. The critical increment calculated from the slope was 69,600.

The reaction curve did not indicate the formation of the intermediate compound $3PbO . 5PbCO_3$ mentioned above. To find an explanation for this fact some experiments were conducted with larger amounts of substance (6-8 gr.) at low temperatures. The result was analogous to the one in the case of ferrous carbonate. Below a certain temperature, in this case, below 308°C. the substance does not decompose totally to form $PbCO_3 . PbO$ but seems to form a solid phase of variable composition with an "active mass" (N) increasing with temperature. The results are given in Table VIII.

TABLE VIII

Temp.		
296°C.	.00173	9 percent
306	.00155	49
316	.00478	50
326	.00780	50

[1] Acta. Univ. Latviensis **11**, 289 (1924).

The product of the first stage of decomposition of lead carbonate $PbO.PbCO_3$ is a white substance. This last compound was decomposed into a reddish-brown oxide, PbO, at considerably higher temperatures. The decomposition was analogous to the case of zinc carbonate, namely, the velocity for about 70 percent of the reaction was constant and then slowed down very appreciably. This stage of the reaction was not investigated carefully enough but Table IX will give an idea of the influence of temperature on this reaction.

TABLE IX

Temp. °C.	Velocity $cm^3/gr.\ min$
426	.49
436	1.32-1.64
446	2.12-2.50
456	3.50-6.15

Another substance investigated by this method was synthetic mercurous carbonate, obtained by precipitation of mercurous nitrate with potassium bicarbonate. The tendency of mercurous nitrate to hydrolyse and form a basic nitrate requires a long period of preparation, during which period the initially white substance turns slightly yellow. The product is not sufficiently pure to yield good results and therefore they will only be described briefly. The description is not omitted because this reaction differs from the previously described by its autocatalytic character.

The velocity of the reaction, very slow in the beginning once started rapidly increases to a maximum and then slows down resembling very much the curves obtained by Lewis[1] for silver oxide. The curve does not yield easily to mathematical analysis. The Ostwald formula could be best tested applying it in this

$$dx/dt = (K_1 + K_2x)(a - x)$$

differential form by plotting $dx/dt : (a - x)$ against x. The plot represented a straight line up to high values of x (a being Hg_2CO_3 and x being Hg_2O or what amounts to the same $- CO_2$). Thus values for K_1 (point where the straight line crosses the axis of ordinates) and K_2, the slope of the line could be calculated. It was found that K_1 is very small[2]. K_2 is large and represents the catalytic effect of mercurous oxide. Unfortunately this substance is unstable, which is evident from the final inclination of the straight line towards the abscissa. Thus, a complication arises on account of the gradual disappearance of the catalyst, ($Hg_2O = HgO + Hg$). The proof of this explanation was obtained by the fact that samples of the remaining oxide showed a largely decreased amount of monovalent mercury and an appearance of metallic mercury in all the cases where the curve had suffered an appreciable inclination towards the abscissa. Another evidence for the autocatalytic character of the reaction is given by the observation that mercurous carbonate

[1] loc. cit.

[2] Lewis in his paper on silver oxide as a matter of fact does not consider it at all, although it could easily explain the asymmetry of his curves.

blackened for an hour in sunshine without a measureable loss of carbon dioxide, decomposed much faster than the pure substance, but the catalytic power of traces of mercurous oxide seems to be confined only to its presence in closest contact, because mixtures of thermally decomposed mercurous carbonate with undecomposed material showed hardly any difference from the pure samples.

Discussion of the Results

The first object of this investigation namely the factors influencing the determination of reaction pressures of carbonates has been solved insofar that it has been shown that the reaction velocities drop logarithmically towards the equilibrium point. The equilibria seem to be obtainable with any thermodynamic degree of accuracy only by increasing the sensitivity of the method so far that they can be attained from both sides. On the other hand the results can be interpreted thermodynamically only when the reactions are known. The cases of lead and cobalt carbonates show definitely that the processes are of a complex nature which must be ascertained before any pressure measurements are made.

There remains to be given a short discussion of the results of the kinetics themselves. The simplest case seems to be zinc carbonate leading to the result that a simple isothermal process of decomposition of a substance having a constant pressure p_s against an outside pressure p is proportional to the pressure difference $(p_s - p)$. As this difference under experimental conditions was constant the reaction velocity was constant also. In the case of ferrous carbonate the pressure of the carbon dioxide changes during the process with change of concentration of carbon dioxide in the solid solution. The reaction constant will be proportional to the constantly diminishing pressure difference and will yield a unimolecular reaction curve in all cases where the reaction is conducted above the temperature where the lowest pressure is one atmosphere. Below this temperature the reaction will have a unimolecular form also, but will go only to a point where the solution pressure will have fallen to one atmosphere. This gives to the value of the difference between unity and "active mass" the meaning of solubility of carbon dioxide at one atmosphere at different temperatures in the solid phase. The solubility increases with decreasing temperature. Lead carbonate undergoes both typical processes described on account of the formation of the intermediate product $PbO \cdot PbCO_3$. In the first stage carbon dioxide is soluble in this intermediate product and yields unimolecular reaction curves; in the second stage $PbO \cdot PbCO_3$ decomposes like zinc carbonate directly into PbO and carbon dioxide. Cobalt carbonate is analogous to the lead salt with the difference that both stages of the reaction are so close together that they can be differentiated only by a kinetic investigation.

The "critical increments", determined from the dependence of the reaction constants on temperature, approximate the value of 80,000 cal. and

seem therefore to be characteristic of the carbonate ion in the crystal lattice[1]. In the case of synthetic ferrous carbonate the value is very much lower probably on account of the catalytic action of water. Catalysed reactions are known to have low temperature coefficients.

I wish to thank Professor G. A. Hulett and Professor H. S. Taylor for the inspiring support and interest in this investigation.

Summary

1. A method is described of investigating reactions of decomposition of solids yielding gaseous reaction products.

2. Ferrous, lead, cobalt, zinc and mercurous carbonates have been investigated by this method with the result that these substances decompose at rates in accord with those found valid for homogeneous unimolecular reactions

3. The mechanisms of decomposition have been derived for all the substances mentioned.

4. All these reactions have high temperature coefficients the mean value for the "critical increment" 80,000 cal., seems to be characteristic of the carbonate ion in the crystal.

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[1] An interesting coincidence may be mentioned here. According to Schaefer and Schubert (Ann. Physik., (4) **50**, 283 (1916)) the carbonate ion in fifteen carbonates investigated by them has three characteristic bands in the infrared with maxima at 6.5, 11.5 and 14.5μ. If we calculate the "activation energy" corresponding to the three bands with the aid of the radiation theory assumption Nhv = E we get in the sum 89.000 cal., a value which is not too far from the observed one.